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PATENT SPECIFICATION

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(54) PHOTOPOLYMERISABLE COMPOSITIONS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London, SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to photopolymerisable compositions comprising one or more materials, which may be monomeric or polymeric, which can be polymerised or cured by treatment with acids. Such materials are commonly referred to, and are referred to herein, as acid-polymerisable or acid-curable materials and examples of suitable materials are epoxide monomers, episulphide monomers, polyepoxides or epoxy resins, polyepisulphides or episulphide resins, phenol/formaldehyde resins, melamine/formaldehyde resins, urea/formaldehyde resins, cyclic ethers and thio-ethers (other than epoxides and episulphides) and polymers thereof, lactones, styrene, vinyl ethers and thio-ethers and resins which contain a cross-linking agent to cross-link or cure the resin when treated with acid. The invention relates in particular to compositions comprising one or more acid-polymerisable or acid-curable materials and at least one photosensitiser which initiates polymerisation or curing of the composition when the composition is exposed to radiation of suitable wavelength.

It is well known that acid-curable resins such as phenol resins and amino resins can be cured by irradiation with ultra-violet, actinic or electromagnetic radiation in the presence of a compound which generates an acid (which term includes Lewis acids) when exposed to ultra-violet radiation. Examples of compounds which have been proposed for use in such compositions are halogen-containing compounds, for example bromoform, carbon tetrabromide, hexabromoethane, 2,5-dimethyl-ω-tribromo-acetophenone, 2,2,2-trichloro-4′-tertiarybutyl acetophenone, halomethylated benzophenones, α-methylol benzoin sulphonic acid esters and aryl diazonium salts of metal halogenides.

It is also well known that epoxy resins can be cured by irradiation in the presence of a substance which generates a Lewis acid when exposed to suitable radiation. Substances which have been proposed for use in epoxy materials include transition metal carbonyls and α,β-unsaturated nitrosamines as well as α-methylol benzoin sulphonic acid esters and aryl diazonium salts of metal halogenides mentioned above. The aryl diazonium salts of metal halogenides have also been proposed for polymerisation of epoxide monomers.

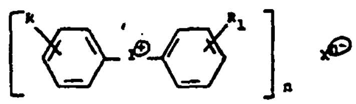
The photosensitive substances proposed hitherto for incorporation in acid-polymerisable or acid-curable materials are activated to release an acid upon exposure to ultraviolet or electromagnetic radiation or actinic radiation comprising a high proportion of ultraviolet radiation. However, the compositions proposed hitherto have not proved satisfactory. Transition metal carbonyls are toxic and slow acting and their use is undesirable. α,β-unsaturated nitrosamines are carcenogenic and slow acting. Use of aryl diazonium salts of metal halogenides results in compositions which polymerise rapidly and which are subject to premature gelation and cannot be stored satisfactorily for any length of time even in the dark. It has been proposed to incorporate stabilizers or gelation inhibitors into epoxy materials containing aryl diazonium salts of metal halogenides in order to inhibit premature gelation of the compositions and confer storage ability in the dark; this increases the cost of the compositions and moreover does not yield entirely satisfactory results even under carefully controlled storage conditions. Moreover the aryl diazonium salts generate nitrogen gas when the composition is irradiated and the resulting cured material may contain undesirable gas bubbles.

We have now found that incorporation of iodonium salts into acid-polymerisable and/or acid-curable materials provides photopolymerisable compositions which overcome the disadvantages of th compositions proposed hitherto. Thus, for example, compositions containing the iodinium salts can be stored for prolonged periods in the dark without notice-

SPECIFICATION AMENDED - SEE ATTACHED

able gelation ccurring and the need to provide gelation inhibitors is obviated.

According to the present invention, there is provided a photopolymerisable composition comprising at least one acid-polymerisable or acid-curable material and as photosensitiser at least one iodonium salt of formula



(I)

wherein n is 1 or 2, R_1 and R_2, which may be the same or different, each is a hydrogen or halogen atom, a nitro group or a hydrocarbon or substituted hydrocarbon group or heterocyclic group, and X^{n-} is an anion derived from an acid which is capable of polymerising or curing the acid-polymerisable or acid-curable material.

Upon exposure of the photopolymerisable composition to radiation of suitable wavelength, the photosensitiser is activated to yield a catalyst species capable of polymerising or curing the composition to yield a polymeric material, and according to a further aspect of the present invention there is provided a process for the preparation of a polymeric material which comprises subjecting a photopolymerisable composition as described in the immediately preceding paragraph to radiation of wavelength such as to activate the photosensitiser and polymerise or cure the composition.

The radiation may be ultraviolet or electron beam radiation or radiation which includes wavelengths in both the visible and the ultraviolet regions of the spectrum. The wavelength of the radiation suitably may be in the range from 200 microns to 600 microns. We prefer to employ radiation of wavelength in the range from 200 microns to 400 microns. Sunlight may be used as the radiation although the optimum wave length of the radiation for any particular composition will depend upon the particular photosensitiser employed in that composition. The optimum wavelength in any particular case is easily determined by simple experiment, for example by determining the electronic absorption spectrum of the photosensitiser.

In the iodonium salts of formula I the groups R and R_1 may be, for example, hydrogen, halogen, nitro, alkyl, cyclo-alkyl, aryl, alkaryl or aralkyl groups or substituted derivatives thereof. Examples of substituents which may be present are halogen, alkoxy, —COOR, —COR, $—NO_2$, —NO, —OH and —SH. In the case where one or both of the groups R and R_1 in the iodonium salt is an alkyl or substituted alkyl group, it may contain from 1 t 20 carbon atoms, preferably from 2 to 6 carbon atoms.

The anion X^{n-} in the iodonium salt may be, for example, a halogen-containing complex ion selected from ClO_4^- and metal or non-metal halogenides. The metal halogenide may be, for example, a polyhalide of boron, antimony, tin, phosphorus, arsenic, bismuth or iron. Examples of suitable anions are tetrafluoroborate III (BF_4^-), hexachloroantimonate V ($SbCl_6^-$), hexafluoroantimonate V (SbF_6^-), hexachlorostannate IV ($SnCl_6^{--}$), hexafluorophosphate (PF_6^-), hexafluoroarsenate (AsF_6^-), tetrachloroferrate III ($FeCl_4^-$) and pentachlorobismuthate III ($BiCl_5^{--}$).

Iodonium salts containing the anions described above, i.e. the perchlorate ion or metal halogenide ions, are suitable for polymerising or curing all types of acid-polymerisable or acid-curable materials. The invention is not restricted, however, to use of iodonium salts containing these anions but includes use of iodonium salts which are capable of polymerising or curing some acid-polymerisable or acid-curable materials but not others. For example, iodonium salts containing halide anions are capable of polymerising or curing urea/formaldehyde resins and melamine/formaldehyde resins but may not satisfactorily polymerise or cure epoxy resins and episulphide resins. The ability of a particular iodonium salt to polymerise or cure a material depends upon the nucleophilicity of its anion; salts containing strongly nucleophilic anions which readily form covalent bonds with carbon atoms to yield stable compounds, for example halide ions, in general will polymerise or cure urea/formaldehyde and melamine/formaldehyde resins but will not polymerise or cure epoxy resins and episulphide resins. Examples of other anions of this type are CF_3COO^-, SO_3F^-, $ArSO_3^-$ (where Ar is an aromatic group, e.g. the toluyl group), HSO_4^-, NO_3^- and the picrate ion. We do not exclude the possibility that some of these anions will provide iodonium salts which will also cure epoxy resins. The ability of a particular iodonium salt to cure a particular material depends upon the ability of the corresponding proton acid, i.e. the proton acid containing the same anion as the iodonium salt, to cure that material. If the proton acid polymerises or cures the material, then the iodonium salt containing the same anion also will be capable of polymerising or curing the material. Thus the suitability of a particular iodonium salt for use with a particular acid-polymerisable or acid-curable material is readily determined simply by mixing the corresponding proton acid with the material.

The iodonium salts used in this invention are normally solids at ordinary temperatures and they are usually incorporated in the acid-polymerisable or acid-curable material in the

form of a solution in an inert liquid diluent, that is a liquid diluent which is chemically inert towards the ingredients of the composition. Any inert liquid diluent in which the iodonium salt is sufficiently soluble may be used, and examples of suitable diluents are halogenated hydrocarbons, e.g. methylene chloride, ketones, e.g. acetone, and alcohols, e.g. ethanol. We prefer to employ a liquid diluent of low boiling point, e.g. below 150°C, in order to facilitate removal of the diluent from the composition. The amount of the diluent used is not critical but preferably is just sufficient to dissolve the appropriate amount of the iodonium salt. After incorporation of the iodonium salt in the composition, the diluent may be removed, if desired, before the composition is irradiated. Removal of the diluent prior to irradiating the composition may be desirable in cases where the diluent is a solvent for the acid-polymerisable or acid-curable material. In the case where the material is, or contains, a monomer, the iodonium salt may be soluble in the material and a diluent may not be required.

The amount of the iodonium salt is not critical but will usually be from 0.01% to 10.0%, and preferably from 0.5% to 5.0% by weight based on the weight of acid-polymerisable and/or acid-curable material in the composition. In general increasing the amount of the iodonium salt results in an increase in the rate of polymerisation or curing achieved although in practice there is little point in using an amount of greater than 10% by weight. The iodonium salt preferably should be soluble in the resin into which it is incorporated and the solubility of a particular iodonium salt in the resin may limit the amount of that salt which can be incorporated. The polymerisation or curing reaction initiated by irradiating the composition is exothermic and use of too large an amount of the iodonium salt may result in a very rapid rise in temperature and loss of control over the reaction conditions. The optimum amount of the iodonium salt will usually be about 3% to 5% by weight but will depend upon the particular salt and acid-polymerisable or acid-curable material employed and the radiation source, and can be determined by simple experiment.

In general, polymerisation or curing of the composition proceeds readily when the composition is irradiated at ambient temperature although the reaction is exothermic and may be accompanied by a rise in temperature of the composition. The rate of polymerisation or curing in general is increased by irradiating the composition at an elevated temperature.

Any acid-polymerisable or acid-curable material may be employed in the present invention. Mixtures of acid-polymerisable and/or acid-curable materials may be employed, as also may mixtures of one or more acid-polymerisable or acid-curable materials and resins which are not acid-curable, for example alkyd resins. Materials containing acid-polymerisable cyclic groups may be employed, notably cyclic ethers for example lactones and acrolein tetramer and especially epoxides and episulphides, and polymers thereof containing polymerisable cyclic groups. Epoxides and episulphides containing from 2 to 20 carbon atoms are suitable, for example ethylene oxide, ethylene sulphide, propylene oxide and propylene sulphide, as also are compounds containing two or more epoxide or episulphide groups. Epoxy and episulphide resins may be used, for example the epoxy resins commonly known as "Araldite" (Registered Trade Mark) epoxy resins. Other acid-curable resins which may be used include phenolic resins, for example phenol/formaldehyde resins, aminoplastics for example urea/formaldehyde and melamine/formaldehyde resins, methylol compounds, methylol ethers of polycarboxylic acid amides, for example derivatives of polyacrylic and polymethacrylic acid amides, alkyd resins containing urethane groups and resins containing carbonic acid esters of N-methylolamides. Acid-polymerisable or acid-curable ethylenically unsaturated materials may also be used, for example styrene, vinyl carbozole, vinyl ethers and diketene (which is both ethylenically unsaturated and a lactone). Resinous materials containing cross-linking agents which can be cured by acids are included.

The compositions of the invention may be used in any of the applications for which acid-curable resin compositions are normally employed, provided that, if the composition is to be polymerised or cured *in situ*, irradiation of the composition is possible. Thus the compositions may be used, for example, for forming surface coatings on a variety of substrates, e.g. wood, paper, metals and textiles, and in printing inks. They may be used as adhesives in applications where they can be subjected *in situ* to radiation, for example in the formation of laminates wherein one or both of the lamina is permeable to radiation, e.g. glass lamina and some plastics lamina. The compositions have the property that only those regions contacted by radiation are polymerised or cured so that they may be used for example in the production of decorative articles having a contoured surface by exposing parts of the surface to radiation to cure those parts and subsequently removing uncured material from the surface. Thus they may be used, for example in the production of printing plates and printed circuits. The c mpositions of the invention may contain foaming agents and they may be foamed prior to irradiating them so that subsequently irradiating them cures or sets the foam.

When a resin composition according to the invention is irradiated, polymerisation or curing commences at the exposed surface and spreads inwardly. The depth of cure achieved is limited by the depth of penetration of the composition by the radiation. This property can be utilised in the production of skinned materials such as skinned foams. Thus for example a foamable resin composition may be irradiated prior to foaming to form a thin surface layer of cured material which is non-foamable and the remainder of the composition may then be foamed to yield a foam having an integral skin. One or more surfaces of the composition may be skinned in this way. Foams having contoured skinned surfaces may be produced.

The compositions of the invention may contain inert fillers and pigments provided these do not prevent penetration of the composition by the radiation used to activate the iodonium salt. If desired, the composition may contain one or more additional photosensitisers, for example to render the composition activatable by radiation which would not activate the iodonium salt in the absence of the additional photosensitiser.

The invention is illustrated but in no way limited by the following examples.

Example 1.

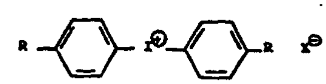
0.3 g of diphenyl iodonium tetrafluoroborate was dissolved in a few ml of acetone and the solution was mixed into 9.7 g of an epoxy resin available as Araldite MY753 epoxy resin from Ciba-Geigy. The mixture was painted on a steel plate and left to stand for 10 minutes to allow the acetone to evaporate, and then the coated plate was exposed to radiation from two 2 kw "Phillips" (Registered Trade Mark) HTQ7 lamp tubes, known as the HTQ light printing lamp, placed at a distance of 8 inches from the plate. The spectral energy output of the lamp, expressed as wavelength in mμ (energy %) was 248 (1.7), 254—8 (3.5), 265 (3.7), 270 (0.7), 275 (0.7), 280 (1.7), 289 (1.0), 2.97 (3.0), 302 (4.7), 313 (12.1), 334 (1.4), 366 (20.6), 405 (6.1), 436 (12.4), 492 (0.7), 546 (11.2), 578 (14.8). After 5 minutes the plate was removed and was found to be coated with a solvent-resistant film of pencil hardness >4H. Solvent resistance was determined by rubbing the film with tissue soaked in acetone 20 times and noting the visible effect, if any, produced by this treatment.

Example 2.

0.3 g of 4,4'-dimethyl diphenyl iodonium hydrogen sulphate was dissolved in a few ml of methanol and the solution was mixed into 9.7 g of a urea/formaldehyde resin-alkyd resin mixture comprising a mixture of 2 parts of butylated urea/formaldehyde and 3 parts of tall oil alkyd in a mixture of solvents (solids content 44% by weight). The mixture was painted onto a steel plate and allowed to stand for 10 minutes to allow the solvent to evaporate and then the painted plate was irradiated as described in Example 1 for 1 minute. A solvent-resistant film of pencil hardness >4H was obtained.

Examples 3 to 8.

These examples illustrate the use as photosensitiser of iodonium salts of formula



wherein the groups R and X are as shown in Table 1 below, employing the procedure described in Example 1. The amounts of the photosensitiser, acetone and resin employed are also given in Table 1, as also is the exposure time required to yield a solvent resistant film of pencil hardness >4H.

TABLE 1

Ex. No.	Group R	Group X	Photo sensitiser (g)	Acetone (g)	Resin (g)	Exposure time (secs)
3	–Cl	AsF_6^-	0.2	0.5	CY179 (6.4)	10
4	$–OCH_3$	AsF_6^-	0.2	0.6	CY179 (6.4)	10
5	–Cl	PF_6^-	0.2	0.6	CY179 (6.4)	20
6	–Cl	AsF_6^-	0.2	0.8	UF/alkyd (7.8)	20
7	$–OCH_3$	SbF_6^-	0.2	0.8	28 (6.4)	20
8	$–CH_3$	PF_6^-	0.2	0.8	CY179 (6.4)	20

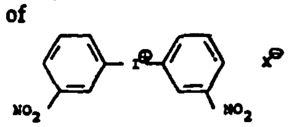
In Table 1:– CY179 denotes an epoxy resin available under the trade name "Araldite" CY179 epoxy resin from Ciba-Geiby.

– UF/alkyd denotes the resin described in Example 2.

– 828 denotes an epoxy resin available under the trade name "Epikote" (Registered Trade Mark) 828 epoxy resin.

Examples 9 to 12.

These examples illustrate the use as photosensitiser of



employing the procedure described in Example 1 except that in Example 12 the source of radiation was changed to a "Thorn" (Registered Trade Mark) 400 w Blue printing lamp.

TABLE 2

Ex. No.	Group X	Photo sensitiser (g)	Acetone (g)	Resin (g)	Exposure time (secs)
9	AsF_6^-	0.2	0.5	CY179 (6.4)	10
10	BF_4^-	0.2	0.8	CY179 (6.8)	90
11	AsF_6^-	0.2	0.6	828 (6.4)	20
12	AsF_6^-	0.2	0.6	828 (6.4)	180

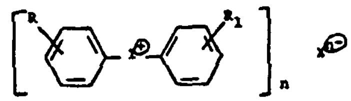
Example 13.

0.2 g of 4-methoxy diphenyl iodonium nitrate dissolved in a few ml of methanol was mixed into 9.8 g of the UF/alkyd resins mixture described in Example 2. The mixture was applied to a steel plate and irradiated as described in Example 1. After exposure to the radiation for 2 minutes, a solvent resistant film of pencil hardness >4H had been produced.

WHAT WE CLAIM IS:—

1. A photopolymerisable composition comprising at least one acid-polymerisable or

acid-curable material and as photosensitiser at least one iodonium salt of formula



wherein n is 1 or 2, R_1 and R_2, which may be the same or different, each is a hydrogen or halogen atom, a nitro group, a hydrocarbon or substituted hydrocarbon group or a heterocyclic group, and X^{n-} is an anion derived from an acid which is capable of polymerising or curing the acid-polymerisable or acid-curable material.

2. A photopolymerisable composition as claimed in claim 1 wherein the amount of the photosensitiser is from 0.01% to 10% by weight based on the weight of the acid-polymerisable or acid-curable material.

3. A photopolymerisable composition as claimed in claim 3 wherein the amount of the photosensitiser is from 0.05% to 5% by weight based on the weight of the acid-polymerisable or acid-curable material.

4. A photopolymerisable composition as claimed in claim 3 wherein the amount of the photosensitiser is from 3% to 5% by weight based on the weight of the acid-polymerisable or acid-curable material.

5. A photopolymerisable composition as claimed in any one of the preceding claims wherein the anion X^{n-} is a halogen-containing complex ion selected from ClO_4^- and metal or non-metal halogenides.

6. A photopolymerisable composition as claimed in claim 5 wherein the anion X^{n-} is a polyhalide of boron, antimony, tin, phosphorus, arsenic, bismuth or iron.

7. A photopolymerisable composition as claimed in any one of the preceding claims wherein the photosensitiser is soluble in the acid-polymerisable or acid-curable material.

8. A photopolymerisable composition as claimed in any one of the preceding claims wherein the acid-curable material comprises an epoxy resin.

9. A photopolymerisable composition as claimed in any one of claims 1 to 7 wherein the acid-polymerisable material is an acid-polymerisable monomer.

10. A photopolymerisable composition substantially as described herein with particular reference to any one of Examples 1 to 13.

11. A polymeric composition derived from a photopolymerisable composition as claimed in any one of claims 1 to 10 by subjecting the photopolymerisable composition to radiation of wavelength such as to activate the photosensitiser and polymerise or cure the composition.

12. A polymeric composition as claimed in claim 11 which is in the form of a surface coating on a substrate.

13. A process for the preparation of a polymeric composition which comprises subjecting a photopolymerisable composition as claimed in any one of claims 1 to 10 to radiation of wavelength such as to activate the photosensitiser and polymerise or cure the composition.

14. A process as claimed in claim 13 wherein the radiation comprises ultra-violet radiation.

15. A process as claimed in claim 13 or 14 wherein the wavelength of the radiation is in the range from 200 microns to 600 microns.

16. A process as claimed in claim 13 substantially as described herein with particular reference to any of the Examples.

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Agent for the Applicants.

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PATENTS ACT 1949

SPECIFICATION NO 1539192

Amendment is made in accordance with the Decision of the Principal Examiner acting for the Comptroller-General, dated the 6th day of June 1979 under Section 8 in the following manner:-

Reference has been directed in pursuance of Section 9 subsection (1) of the Patents Act 1949 to Patent Nos 1491539 and 1516351.

THE PATENT OFFICE
15 June 1979

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